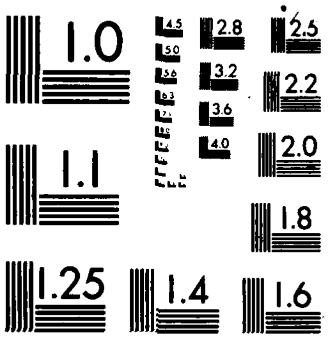
AD-A141 502 A TWISTED P-C DOUBLE BOND: SYNTHESIS AND STRUCTURE OF A (METHYLENE)PHOSPH..(U) TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY R H NEILSON ET AL. 18 MAY 84 1/1

UNCLASSIFIED TCU/DC/TR-84-05 N00014-79-C-0632 F/G 7/2 NL



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OFFICE OF NAVAL RESEARCH

Contract No. N00014-79-C-0632

Task No. NR-053-720

TECHNICAL REPORT NO. TCU/DC/TR-84-05

A Twisted P-C Double Bond: Synthesis and Structure of a (Methylene)phosphine·$Fe(CO)_4$ Complex

by

R.H. Neilson, R.J. Thoma, I. Vickovic, W.H. Watson

Prepared for Publication

in

Organometallics

Texas Christian University
Chemistry Department
Fort Worth, TX 76129

May 18, 1984

84 05 29 004

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER TCU/DC/TR-84-05	2. GOVT ACCESSION NO. AD-A141502	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A Twisted P-C Double Bond: Synthesis and Structure of a (Methylene)phosphine$\cdot Fe(CO)_4$ Complex		5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1983
		6. PERFORMING ORG. REPORT NUMBER TR-84-05
7. AUTHOR(s) R.H. Neilson, R.J. Thoma, I. Vickovic, W.H. Watson		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0632
9. PERFORMING ORGANIZATION NAME AND ADDRESS Texas Christian University Fort Worth, TX 76129		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-720
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research		12. REPORT DATE May 18, 1984
		13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Organometallics

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

amino(methylene)phosphine
(methylene)phosphine
phosphine-iron complex

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reaction of $(Me_3Si)_2C{=}PCl$ with $LiN(SiMe_3)_2$ affords the tetrasilylated amino(methylene)phosphine 1 which, reacts smoothly with $Fe_2(CO)_9$ yielding the η^1 complex $(Me_3Si)_2C{=}P[Fe(CO)_4]-N(SiMe_3)_2$ (2). X-ray crystallographic analysis of 2 reveals an unusual coordination of the phosphine ligand in an equatorial position as well as a short (1.657 Å), but severely twisted (30.3°), P=C double bond.

DD FORM 1473, 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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Summary: The reaction of $(Me_3Si)_2C{=}PCl$ with $LiN(SiMe_3)_2$ affords the tetrasilylated amino(methylene)phosphine 1 which, reacts smoothly with $Fe_2(CO)_9$ yielding the η^1 complex $(Me_3Si)_2C{=}P[Fe(CO)_4]{-}N(SiMe_3)_2$ (2). X-ray crystallographic analysis of 2 reveals an unusual coordination of the phosphine ligand in an equatorial position as well as a short (1.657 Å), but severely twisted (30.3°), P-C double bond.

●● ●● A141502 (U) FIELD/GROUP ●●●●●●

UNCLASSIFIED TITLE

A TWISTED P-C DOUBLE BOND: SYNTHESIS AND STRUCTURE OF A (METHYLENE)PHOSPHINE FE(CO)4 COMPLEX.

ABSTRACT

(U) THE REACTION OF (ME3SI)SC=PCL WITH LIN(SIME3)2 AFFORDS THE TETRASILYLATED AMINO(METHYLENE)PHOSPHINE 1 WHICH, REACTS SMOOTHLY WITH FE2(CO)9 YIELDING THE ETA SUPER 1 COMPLEX (ME3SI)2C=P(FE(CO)4)-N(SIME3)2 (2). X-RAY CRYSTALLOGRAPHIC ANALYSIS OF 2 REVEALS AN UNUSUAL COORDINATION OF THE PHOSPHINE LIGAND IN AN EQUATORIAL POSITION AS WELL AS A SHORT (1,657 A), BUT SEVERELY TWISTED (30.3 DEG), P = C DOUBLE BOND. (AUTHOR)

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EQUATORIAL POSITION
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PHOSPHINE LIGAND
  USE LIGANDS
      PHOSPHINE

X-RAY CRYSTALLOGRAPHIC ANALYSIS
  USE CRYSTALS
      X RAYS

METHYLENE
  USE METHYLENES

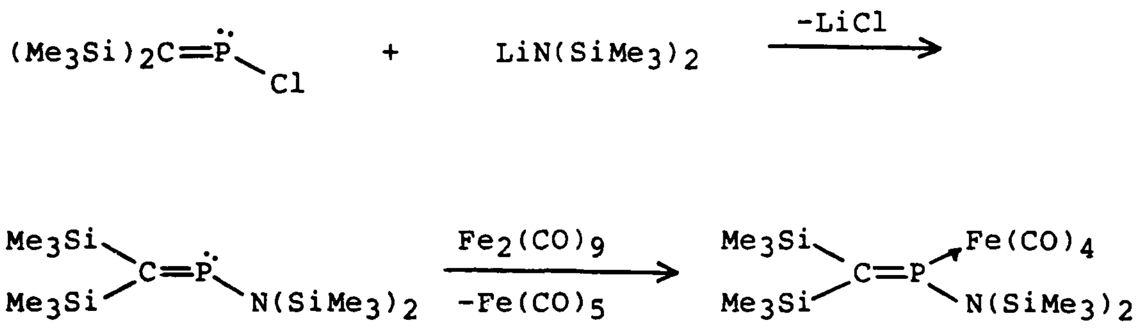
SYNTHESIS
  USE SYNTHESIS

PHRASES NOT FOUND DURING LEXICAL DICTIONARY MATCH PROCESS

AMINO METHYLENE PHOSPHINE 1
SUPER 1
PHOSPHINE FE CO 4
30.3 DEG

The high level of current interest in unusually-hybridized phosphorus compounds has been stimulated, in part, by their potential as new types of ligands in organometallic chemistry. Among the methylenephosphines, $RP{=}CR_2$, for example, both σ (η^1) and π (η^2) complexes of the $-P{=}C\langle$ moiety are now known.[1,2] With two exceptions[2], however, all of the methylenephosphine complexes have contained the same ligand, $MesP{=}CPh_2$, first reported by Bickelhaupt.[3] In order to extend these studies to the use of other ligands, we have begun an investigation of the coordination chemistry of our recently prepared amino(methylene)phosphines[4]. We report here the synthesis of the new methylenephosphine $(Me_3Si)_2NP{=}C(SiMe_3)_2$ and its iron tetracarbonyl complex which is found to have an unusually twisted phosphorus-carbon double bond.

Treatment of lithium bis(trimethylsilyl)amide (68 mmol) in Et_2O (250 mL) at 0^oC with chloro[bis(trimethylsilyl)methylene]-phosphine[5] (68 mmol) afforded the tetrasilylated amino(methylene)phosphine **1** as a distillable yellow liquid (bp 61-63^oC/0.01 mm) in 59% yield. A purified sample of **1** (ca. 5 mmol) was then allowed to react with one equivalent of $Fe_2(CO)_9$ in pentane (25 mL) at room temperature with stirring for 18 hours. Quantitative formation of the phosphine$\cdot Fe(CO)_4$ complex was shown by ^{31}P NMR spectroscopy, and **2** was isolated as dark orange crystals (mp 153-155^oC) by slow evaporation of the solvent. In addition to NMR spectroscopy (Table I), compounds **1** and **2** were characterized by satisfactory elemental analysis.[6]



1 2

Several aspects of the NMR spectra of 1 and 2 are structurally diagnostic. First, the low-field ^{31}P and ^{13}C chemical shifts in both compounds are indicative of sp^2 hybridization and strongly suggest η^1-coordination to $Fe(CO)_4$ via the phosphorus lone pair. Second, non-equivalence of the C-bonded Me_3Si groups due to hindered rotation about the P=C double bond is seen in the ^1H, ^{13}C, and ^{29}Si NMR spectra. Third, there is a substantial coupling ($^2J_{PC}$ = 18.6 Hz) between phosphorus and the carbonyl carbons of the $Fe(CO)_4$ group, indicating that 2 does not undergo the rapid intermolecular exchange of CO as observed for the analogous complexes of the isoelectronic aminophosphenium ions.[7]

The X-ray crystallographic analysis[8] of 2 (Figure 1) confirms the η^1-coordination mode of the (methylene)phosphine and reveals some unexpected features. Most significant is the severe twist about the P=C bond of 30.3(6)$^\circ$; however, the P-C bond distance of 1.657(5) Å is significantly shorter than the 1.68 to 1.72 Å range reported by Appel[9] for a series of planar P=C

π-systems. The distance is equivalent to the 1.647(9) Å and 1.657(4) Å values reported recently for some 3-coordinate (methylene)phosphoranes.[10,11] Steric interactions between the bulky substituents are relieved by a rotation about the P=C bond. Although the P=C bond is considerably longer than a C=C bond, the present structure is indicative of the interactions which would exist in tri- and tetraisobutylethylenes.

In contrast to most simple phosphine·$Fe(CO)_4$ complexes,[12,13] the ligand is coordinated at an equatorial site in a slightly distorted trigonal bipyramidal geometry around the iron. The Fe, P, C(2), and C(4) atoms are coplanar with a maximum deviation from the plane of 0.001 Å. In the trigonal plane, the P-Fe-C angles are 124.1(3) and 125.5(3)$^{\circ}$ while the C-Fe-C angle is compressed to 110.4(3)$^{\circ}$. The two axial ligands make a C-Fe-C angle of 173.1(4)$^{\circ}$ and are bent toward the phosphine ligand which, to our knowledge, is unprecedented. The angles between axial and equatorial ligands range from 86.8(2) to 94.7(3)$^{\circ}$. All three atoms in the N-P=C linkage have trigonal planar geometries with the Si_2N and Si_2C planes being nearly orthogonal. The NPC plane lies between the axial and equatorial planes of the $Fe(CO)_4$ moiety, probably to further minimize steric interactions.

Acknowledgment. The financial support of the U.S. Office of Naval Research and The Robert A. Welch Foundation (P-074 and P-759) is gratefully acknowledged. Silicon-29 NMR spectra were kindly provided by Professor Lattman at Southern Methodist University.

TABLE I. NMR Spectroscopic Data[a]

	1	2
δ ^{31}P	383.1	311.4
δ ^{1}H (J_{PH})		
$N(SiMe_3)_2$	0.16 (0.5)	0.32
$C(SiMe_3)_2$[b]	0.12 (2.1)	0.15
	0.15	0.25
δ ^{13}C (J_{PC})		
$N(SiMe_3)_2$	3.90 (1.9)	2.99 (2.0)
$C(SiMe_3)_2$[b]	3.05 (7.8)	-0.10 (14.6)
	3.64	2.26 (4.9)
P=C	187.5 (96.7)	162.1 (12.6)
CO		213.6 (18.6)
δ ^{29}Si (J_{PSi})		
$N(SiMe_3)_2$	1.42	7.90 (5.0)
$C(SiMe_3)_2$[b]	-4.60 (39.3)	-5.30 (15.8)
	-9.84 (10.7)	-8.00 (19.4)

[a] Chemical shifts downfield from Me_4Si for ^{1}H, ^{13}C, and ^{29}Si, and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C, ^{31}P, and ^{29}Si, $CDCl_3$. [b] Non-equivalent Me_3Si groups due to hindered P=C bond rotation.

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6. Compound 1: Anal. Found: C, 44.37; H, 10.58. Calcd for $C_{13}H_{36}NPSi_4$: C, 44.64; H, 10.37. Compound 2: Anal. Found: C, 39.17; H, 7.00. Calcd for $C_{17}H_{36}FeNO_4PSi_4$: C, 39.45; H, 7.01.

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8. Crystal of dimensions .17 x .34 x .41 mm, triclinic space group $P\bar{1}$ with a = 10.567(3), b = 15.129(7), c = 10.562(3) Å, α = 97.44(3), β = 115.50(2), γ = 106.08(3)°, V = 1403(1) Å^3, Z = 2, μ(calcd) = 1.225 gcm^{-3}, F(000) = 548, λ(CuK) = 66.5 cm^{-1}. 3831 independent reflections collected by θ:2θ scan technique on Syntex P2$_1$ diffractometer, 3036 were considered observed ($I > 3\sigma(I)$). Lorentz and polarization corrections, but no absorption corrections. Anisotropic refinement (H atom positions fixed, thermal parameters isotropic) led to R = 0.051 and R_w = 0.062 where $w = 1/\sigma^2(F_o)$. Scattering factors and real and imaginary anomalous dispersion corrections Cromer, D.T.; Mann, J.B. Acta Cryst. 1968, A24 321. Atomic coordinates, thermal parameters, bond length, and valence angles are listed in supplementary Tables 1-5. Lists of structure factors are also available.

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10. Appel, R.; Knoch, F.; Kunze, H. Angew. Chem., Int. Ed. Engl. 1984, 23, 157.

11. Caira, M.; Neilson, R.H.; Watson, W.H.; Wisian-Neilson, P.; Xie, Z.-M. J. Chem. Soc., Chem. Commun., in press.

12. Axial substitution is very common for phosphine·$Fe(CO)_4$ complexes. For example, see the following and references cited therein. Keiter, R.L.; Rheingold, A.L.; Hamerski, J.J.; Castle, C.K. Organometallics 1983, 2, 1635.

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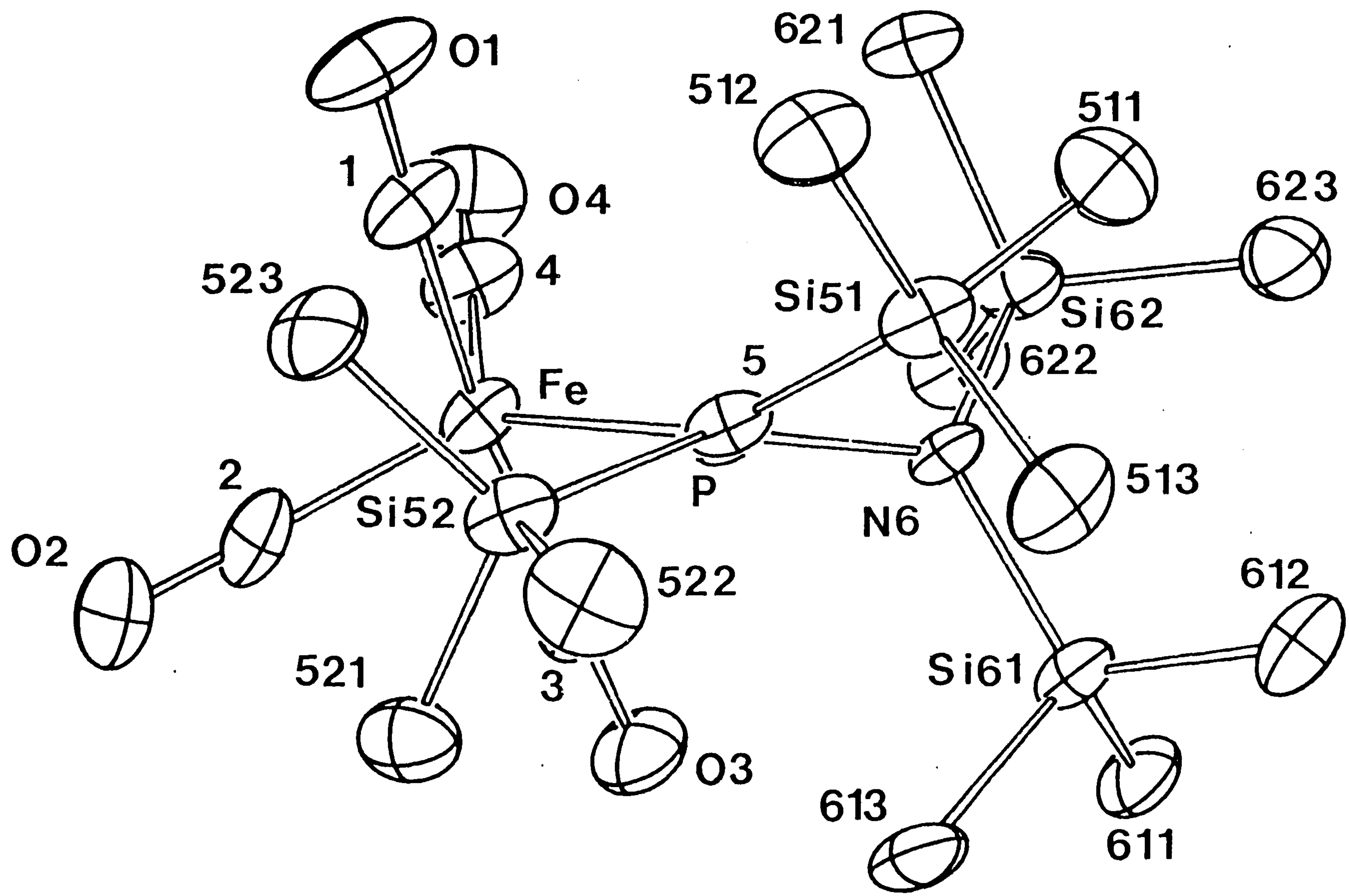
Figure 1. Ortep drawing of 2 viewed down the C(5)=P bond. Thermal elipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (°): P-Fe 2.208(2); Fe-C(1) 1.795(4); Fe-C(2) 1.794(2); Fe-C(3) 1.787(4); Fe-C(4) 1.768(7); P=C 1.657(5); P-N 1.681(4); N-Si 1.788(4); 1.790(4); C(5)-Si 1.884(7), 1.890(6); Fe-P-C(5) 128.0(2); Fe-P-N 116.8(2); N-P-C(5 115.2(8); P-C(5)-Si(51) 135.0(7); P-C(5)-Si(52) 118.7(3).


O1
1
O4
4
523
Fe
2
O2
Si52
521
3
522
O3
5
P
512
621
Si51
511
623
Si62
622
513
N6
612
Si61
613
611

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